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POSSIBILITIES OF BROMINATED FLAME RETARDANTS EXTRACTION FROM POLYMERS OF E-WASTE

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SUMMARY: For sound management practices, the quantification of brominated flame retardants (BFRs) in e-waste is necessary for avoiding harmful emissions during recycling process and mitigation phenomena in new products. This research focuses on assessing the content of tetrabromobisphenol-A (TBBPA) in ABS (acrylonitrile-butadiene-styrene), PP (polypropylene), PC (polycarbonate) and polymer blends (PC/ABS etc.) from a total of 36 plastic housing e-waste samples. Plastic parts from microwave ovens, irons, vacuum cleaners and DVD/CD players are subjected to microwave-assisted (MAE) and ultrasound-assisted extraction (UAE) system. It is conducted that the detection of the target compound depends on (a) the polymeric matrix, (b) the extraction solvent, (c) the extraction method and most important (d) the type of the e-waste examined. Regarding the extraction methods, results show that MAE offers satisfactory extraction of TBBPA amount from ABS, while UAE characterized as relatively insufficient. Though, different solvent means are examined for optimizing the conditions of UAE. Focusing on ABS and PP polymers, higher amount of TBBPA is obtained using a binary solvent mixture, isopropanol:*n*-hexane (1:1) whereas isopropanol exhibited incomplete extraction.

1. INTRODUCTION

Due to the exponential increase of electronics markets and industry demands, the waste e-plastics are currently produced, used and discarded requiring environmentally-sound management practices and boosting of recycling. By the end of 2018, more than 10 million tonnes of plastic would have been produced globally from a total of 50 million tonnes e-waste (Markowski, 2015). European Commission promotes a strategy with a more ‘circular’ approach for plastics that comprises the overall impacts (economic, environmental and social) of using recycled WEEE plastics towards sustainability (European Commission, 2018). Improvements in recycling techniques that turn the waste polymeric parts into new polymer products (Taurino et al., 2010) or allows feedstock recovery for chemicals/monomers/fuels production (Datta and Kopczyńska, 2016) could contribute to high-grade products with economic and environmental benefits.

However the diversity among product types and mainly the inherent characteristics of plastic that contain numerous additives, both organic and inorganic, including pigments, halogenated flame retardants (FRs), various colorants, plasticizers or stabilizers (Martinho et al., 2012; Zhao et al., 2017), raise specific challenges for waste management. Specifically, FRs are further classified as containing either chlorine or bromine, namely chlorinated flame retardants (CFRs) and brominated flame retardants (BFRs), with the last ones to be the most widespread within the electric and electronic appliances. Review studies state that corrosive gases like HCl and HBr are released from halogenated plastics during the processing and management methods applied in WEEE recycling units (e.g. during the application of thermal methods) (Oleszek et al., 2013). Moreover, according to literature data, certain BFRs, amongst them tetrabromobisphenol A (TBBPA), have previously been reported to be transferred into new recycled products with sensitive end uses (Hahladakis et al., 2018). In this sense, efforts are being made to develop ways for screening material prior to recycling process and then removing BFRs from the plastic articles during recycling stage (Paine et al., 2014).

Several techniques have been developed for the extraction of BFRs from e-scrap plastic among them supercritical-fluid extraction (SFE), soxhlet extraction, pressurised liquid extraction (PLE), ultrasonic-assisted extraction (UAE), and microwave-assisted extraction (MAE) (Schlummer et al., 2007; Chen et al., 2012; Wäger et al., 2011; Miyake et al., 2017; Vilaplana et al., 2009).

This research focuses on the extraction of TBBPA from plastic parts of devices grouped in certain e-waste categories (cat. 1, 2 and 4 as defined by Directive 2012/19/EU). Those e-waste were selected since household appliances constituent the great majority of WEEE plastic. Two extraction methods were chosen for the implementation of removal, assisted by microwaves or ultrasonication as both of them are considered environmentally-sound methods referring to the energy consumption and to the volume of solvents consumed as reagents (Bart, 2005). Hence, the main focus is to (a) provide both qualitative and quantitative investigation of TBBPA in plastic fractions (b) discuss the challenges in the field of BFRs extraction from polymeric matrices and provide recommendations for future research.

2. MATERIALS AND METHODS

For the purpose of the study, a total of 36 plastic housing samples were collected from 3 different categories as mentioned in Directive 2012/19/EU. Particularly, (i) 9 samples from microwave ovens, (ii) 7 and 16 samples from post-consumers irons and vacuum cleaners, respectively and, (iii) 4 samples from DVD/CD players were selected to undergo chemical extraction and analysis for TBBPA content. The highest number of plastic samples was made from the copolymer ABS ($n = 20$) and PP ($n = 14$) polymer type. The plastic components were manually chopped into foils to a size of less than 2×1 mm; then, the foils were embattled with liquid nitrogen to further reduce the particle size (less than 1 mm). Afterwards, the samples were stored in the dark at a temperature of 25 ± 2 °C. The data characteristics of samples are summarized in Table 1.

For the extraction of TBBPA, two approaches were employed, namely ultrasonic-assisted extraction (UAE) and microwave-assisted extraction (MAE). A number of samples (7 out of 36) were subjected to both extraction processes in order to first compare their efficiency and then recommend the optimal approach which may differ from polymer to polymer. Therefore, for the comparison approach between the extraction methods, material size dimension and solvent media were kept stable, in a way to focus on specific parameters, referring to the extraction technique. To estimate, the diffusion and the mass transfer of target compound from matrices into the solvent media under sonication, the optimization of UAE method followed. Different solvent media were examined (polar and polar/non polar mixture) in function with the type of polymer (ABS, PP). Thus, the plastic chops were subjected to (i) UAE and (ii) MAE systems using (a) isopropanol (HPLC grade, Chem-Lab NV)

and *n*-hexane (HPLC grade, Sigma-Aldrich) (1:1 v/v) and (b) isopropanol (HPLC grade, Chem-Lab NV), as organic solvents taking also into account the available literature data. The isopropanol solvent media was used for optimizing only the extraction of TBBPA by ultrasonication.

Table 1. Description of the e-plastic samples examined.

Category of e-waste according to Directive 2012/19/EU	Sample type	Sampling No.	Description	Category of e-waste according to Directive 2012/19/EU	Sample type	Sampling No.	Description
Category 1. Large household appliances	Microwave ovens	M1	ABS	Category 2. Small household appliances	Vacuum cleaners	V1	ABS
		M2	ABS			V2	PP
		M3	ABS			V3	ABS
		M4	ABS			V4	ABS
		M5	PP			V5	PP
		M6	ABS			V6	ABS
		M7	PC/ABS			V7	PP TD10
		M8	PP-MD20			V8	ABS
		M9	PP-MD20			V9	ABS
Category 2. Small household appliances	Irons	IR1	PP			V10	ABS
		IR2	PC			V11	ABS
		IR3	PP			V12	PP
		IR4	PP			V13	ABS
		IR5	PP			V14	ABS
		IR6	PP			V15	PP
		IR7	PP			V16	ABS
Category 4. Consumer electronics	DVD/CD players	CD1	ABS				
		CD2	ABS				
		CD3	ABS				
		CD4	ABS				

UAE was performed using an ultrasonic bath (Falc Instruments, 4.5L bath volume, 40-59 KHz). Regarding experiments, 1 g of each sample was transferred into a 50 mL glass reagent bottle. Then, 30 mL of a solvent mixture consisting of isopropanol/*n*-hexane (IP/*n*-hexane, 1:1, v/v) either isopropanol (IP). After samples' immersion (24 h), the bottles were submerged halfway into the water of the ultrasonic bath. For achieving maximum extraction of TBBPA, samples left under ultrasonic irradiation (40 KHz) thrice for 30 min. All extracts collected were filtered through a PTFE syringe filter 25 mm of a 0.45 µm pore size (Lab Solutions, Greece). Afterwards, the extracts were then concentrated under a gentle blow of nitrogen working along with mild heating produced by a controlling dry bath in the bottom (heating reactor). The residue was resolved with acetonitrile to achieve a volume of 5 mL and was placed in amber glass vials. The concentration of TBBPA was determined with high-performance liquid chromatographer (Waters Alliance 2695 HPLC system) connected with a diode-array detector (DAD) (Waters 2996 PDA detector). The detection limit was 250 ng/g by using HPLC-DAD analysis method.

The MAE procedure was carried out for approximately 1 g of solid sample and addition of 20 mL of isopropanol/*n*-hexane (IP/*n*-hexane, 1:1, v/v) into the closed vessels designed for microwave sample preparation system (Multiwave 3000, Anton Paar, Graz, Austria). The produced extracts were subjected to centrifugation at 2500 rpm for 5 min. After decanting the liquid phase, a mixture of deuterated ¹³C₁₂-TBBPA was introduced in the vial. In order to reduce the volume to 1.5 mL, a water-bath rotary evaporator (Rotavapor R-205, Büchi, Switzerland) was operated at 40 °C. The collected extracts were filtered using mini uniprep 0.2 µm pore polypropylene (PP) filter vials (Whatman, UK) before analysis with a high-performance liquid chromatographer (HPLC) coupled to a tandem mass spectrometer (MS) (HPLC/MS). The detection limit was 50 ng/g.

3. RESULTS AND DISCUSSION

3.1. TBBPA content range in household e-waste plastics

From 36 samples in total, TBBPA could be detected in 21 samples using HPLC-DAD or HPLC/MS. The results show that concentration levels of TBBPA vary significantly among the samples, even if it refers to the same category of waste, ranging from values below the detection limit to the maximum value of 3109 $\mu\text{g/kg}$ (Figure 1), while the median value was calculated 250 $\mu\text{g/kg}$. A slight primacy of the TBBPA content in samples from vacuum cleaners and DVD/CD players was indicated. Particularly, the mean values of TBBPA detected in housing plastics per kind of e-waste, present the follow descending order: (a) DVD/CD players (1146 $\mu\text{g/kg}$); (b) vacuum cleaners (754 $\mu\text{g/kg}$); (c) irons (677 $\mu\text{g/kg}$) and (d) microwave ovens (350 $\mu\text{g/kg}$).

The presence of TBBPA in small household appliances (vacuum cleaners, toasters etc.) have been proved in previous studies in a range of 100 to 3700 mg/kg (Wäger, et al., 2011); thus, the values provided by the present research were comparatively trending down. Overall, a direct comparison between the current study and previous studies is rather difficult and complex due to the different parameters used for the preparation of samples, extraction method and analysis technique applied.

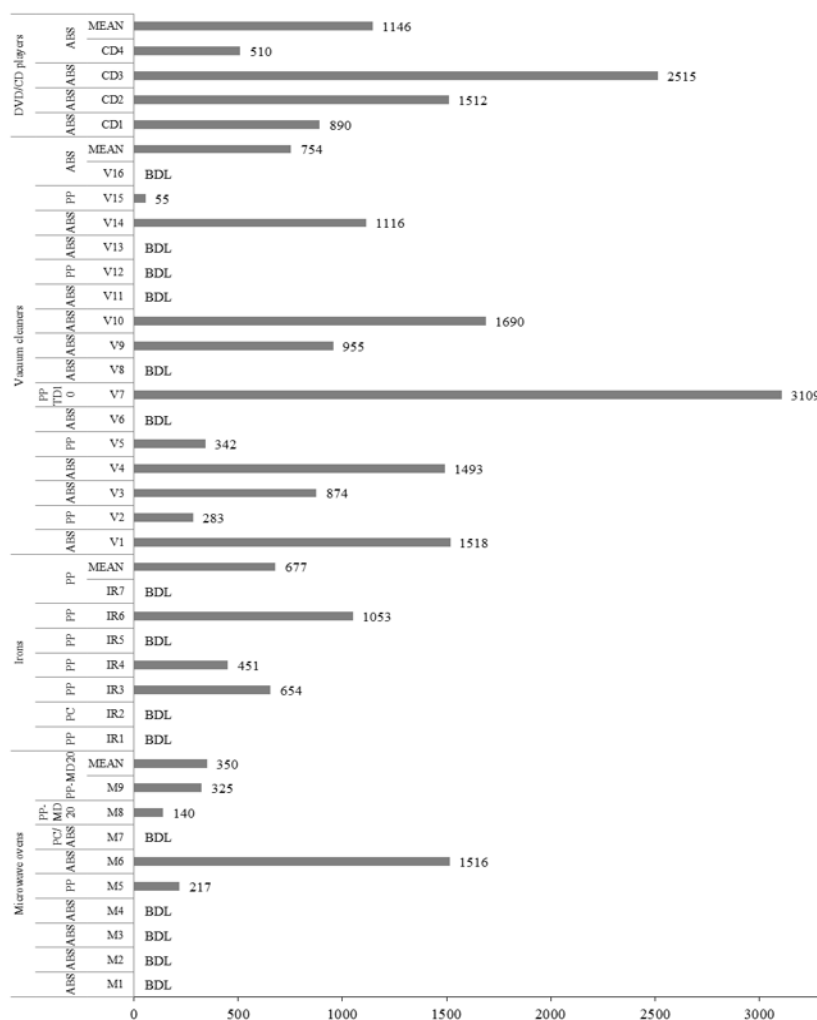


Figure 1. TBBPA values in e-waste plastics examined ($\mu\text{g/kg}$). BDL refers to the values that are below the detection limit of the analysis method.

3.2. TBBPA content range per type of polymer

Figure 2 presents the content range of TBBPA per polymer type and the minimum, maximum, mean value, upper and lower quartiles are shown in the chart. As illustrated, the range of TBBPA per polymer type shows differences among the three groups evaluated. The mean value of TBBPA compound was found higher in ABS (1225 $\mu\text{g/kg}$) than in PP (372 $\mu\text{g/kg}$). On the contrary, it was found that in polymers made from PC and PC blend with ABS, TBBPA has not incorporated for flame retardancy. This could be maybe attributed to the use of different kind of FRs in the certain polymer type. Although, uncertainties rely on the limited number of PC samples that were available for testing ($n=2$). Comparing the results with other studies (Yu et al., 2013) differential values were also found in the articles obtained for TBBPA quantification.

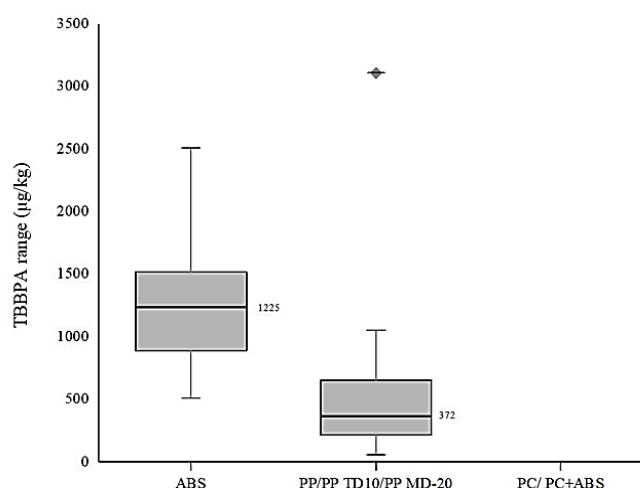


Figure 2. Mean and TBBPA content ranges in plastic matrices ($\mu\text{g/kg}$) calculated separately per polymer type.

3.3. Comparison between MAE and UAE methods efficiency

For the evaluation of the amount of TBBPA extracted, ABS copolymers (V1, V3, V4) and PP polymers (V2, V7, V12, M8) were introduced in both UAE and MAE system, using as solvent media isopropanol/*n*-hexane (1:1, v/v). The results obtained are presented in Figure 3. Results demonstrated that a significantly higher degree of extraction was exhibited under microwave irradiation regarding samples made from ABS. TBBPA amount levels were detected to be about 29, 61 or 100% elevated in ABS matrices (namely V3, V4, V1) subjected to microwave irradiation extraction. On the other hand, a diversionary result in the amount extracted from PP was found in the case of sonication.

One of the most crucial steps for determination of TBBPA remains its chemical extraction from the polymeric matrix. Parameters like the nature of the extractive solvents, the operated temperature, time and the particle size of the matrices have to be thoroughly considered in order to understand how the extraction yield could be influenced in a liquid-solid extraction method (Vilaplana et al., 2009; Zhang and Zhang, 2012). Since on samples undergoing in both methods, a question was raised whether the differences found between the TBBPA amounts extracted could be explained predominately by the type of polymer and to what extent contribution was made by extracting conditions. For that reason, significant references were evaluated on the matter. Zhang and Zhang, (2012) highlighted that intermolecular bonds between TBBPA and matrix could break more easily when the extraction is carried out at relatively high temperatures. In this study MAE has operated in higher temperatures during extraction in contrary with UAE. In that case, the diffusion rate even in the plastic core or the boundary layer around the polymer surface become faster as the temperature

risers. Moreover, the extraction temperature may enhance the mass transfer to the solvent media due to the swelling effect of the polymer (Vilaplana et al., 2009). Additionally, Covaci et al. (2009) has reported that the incorporation of FRs into polymers may influence the feasibility of BFRs quantification by embedding or accelerating the extraction and then analysis processes. In the same manner, Miyake et al. (2017) underlined that BFRs content upon UAE could be underestimated in a complex sample matrix as the inadequate disintegration of polymer structure maybe hinder the complete extraction. As a result, the evaluation of applicability of the certain experimental approaches may contain underestimation or overestimation of actual amounts of TBBPA presented in our complex samples and the evaluation of the findings lies in explaining the effect of extraction methods.

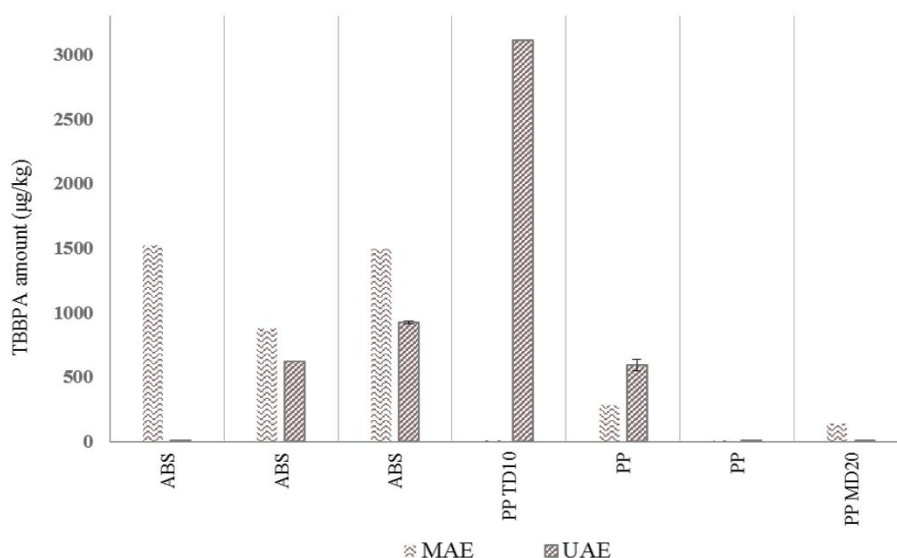


Figure 3. Amount of TBBPA extracted from ABS copolymers and PP polymers by using MAE and UAE method. Error bars represent one standard deviation.

3.4. Effect of extractive solution in UAE system

In order to optimize the efficiency of ultrasonic irradiation to extract TBBPA from plastics, certain samples were treated with different solvent media, (a) IP/*n*-hexane, 1:1, v/v and (b) IP. The selected samples were marked as ABS (n=6), PC (n=1), PP (n=3), PP TD10 (n=1) and PP-MD20 (n=2).

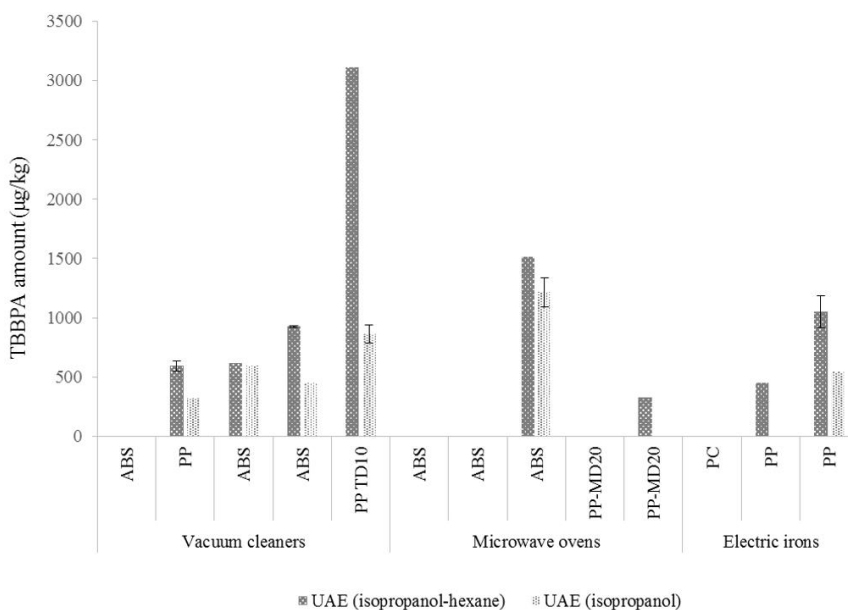


Figure 4. Dependence of the TBBPA extraction efficiency on the solvents media, isopropanol-hexane and isopropanol using UAE method. Error bars represent one standard deviation.

A polar solvent, like isopropanol, was chosen since the hydroxyl groups tend to make the compound molecule more polar and may enhance the solubility of TBBPA (Xie et al., 2007). Accordingly to the results (Figure 4), the measured amount of TBBPA upon the procedure, in case of using as extraction solvent only IP, was found to be significantly decreased. Particularly, the recovery of TBBPA from ABS was reduced about 4 to 51% with IP. Meanwhile, immersion in isopropanol solution affected the extraction level of TBBPA in PP polymers (PP, PP-MD20, PP TD10) whereas a decrease of about 46 to 100% was shown.

The efficiency of the mixture of solvents could be explained by the positive effect of *n*-hexane which accelerates the diffusion of TBBPA from the polymer structure by swelling mechanism (Bart, 2005). In brief, despite the fact that the performance of UAE was not optimal in relation with MAE, the solvent mixture of IP/*n*-hexane resulted in the satisfactory recovery of TBBPA compared to the isopropanol solvent media.

4. CONCLUSIONS

The main aim of this study was to investigate the presence of TBBPA in plastic fractions from microwave ovens, electric irons, vacuum cleaners and DVD/CD players. The determination of BFRs in plastics from WEEE becomes crucial due to (a) the heterogeneity of polymers used and (b) the complex intrinsic characteristics that polymeric matrix exhibit. Hence, their extraction depends on various parameters and makes difficult the development of universal methods of extraction and analysis. Among the findings of the present research, it was revealed that the content of TBBPA varies from plastic to plastic even among the same category of waste. Both MAE and UAE methods were applied for the extraction of TBBPA with MAE to exhibit higher recovered amounts of TBBPA when a solvent media of isopropanol and hexane were used due to the operational temperature that enhanced the diffusion rates. Despite the fact that the performance of UAE was not optimal, the binary mixture of alcohols and alkanes was considered as the most suitable solution. Besides the evidences from this study, future research needs to be done for the maximum recovery of TBBPA in complex matrices by MAE and UAE.

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